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NEW DATA ON METACINNABAR FROM TUSCANY (ITALY)

Abstract - C. Biagioni, S. Musetti, M. Pasero, *New data on metacinnabar from Tuscany (Italy).*

New crystallographic data collected on samples of metacinnabar from the Levigliani mine (Apuan Alps), Niccioleta mine (Metalliferous Hills), and the Monte Amiata Hg ore district are reported. The study of the samples from Levigliani completes the characterization of this phase, integrating the data already available in literature. Its crystal structure has been refined on the basis of single-crystal X-ray diffraction data, achieving a R_1 factor = 0.044 on the basis of 43 reflections with $F_o > 4\sigma(F_o)$. The crystal structure refinement confirms the substitution of Hg by Zn and Fe as well as the contraction of the unit-cell parameter [a = 5.7966(8) Å]. Samples from southern Tuscany do not show any significant chemical substitution. Metacinnabar from the Niccioleta mine was identified on the basis of X-ray powder diffraction only, due to the microcrystalline nature of the available material. The unit-cell parameter was refined on the basis of powder data [a = 5.859(1) Å]. Samples from the Monte Amiata Hg ore district were collected in the Bagnore and Pietrineri mines. Their unit-cell parameters, refined on the basis of single-crystal X-ray diffraction data, are a = 5.8358(14) Å (Bagnore) and 5.8355(5) Å (Pietrineri). The refinement of the crystal structures of samples from Bagnore and Pietrineri converged to R_1 = 0.037 and 0.026, respectively. The occurrence of metacinnabar in the ore deposits from Tuscany can be interpreted as an evidence for relatively high temperatures (> 315°C) locally attained during Hg ore formation.

Key words - metacinnabar, crystal structure, mercury, sulfide, Apuan Alps, Monte Amiata, Metalliferous Hills, Tuscany, Italy

Riassunto - C. Biagioni, S. Musetti, M. Pasero, *Nuovi dati sul metacinabro toscano.*

Vengono riportati nuovi dati cristallografici su campioni di metacinabro provenienti dalla miniera di Levigliani (Alpi Apuane), dalla miniera di Niccioleta (Colline metallifere) e dal distretto mercurifero del Monte Amiata. Lo studio dei campioni di Levigliani completa la caratterizzazione di questa fase, integrando i dati già disponibili in letteratura; la struttura del metacinabro di questa località è stata raffinata sulla base di dati di cristallo singolo fino a un fattore di accordo R_1 = 0.044 sulla base di 43 riflessi con $F_o > 4\sigma(F_o)$. Il raffinamento strutturale conferma la sostituzione di Hg da parte di Zn e Fe e la contrazione del parametro di cella [a = 5.7966(8) Å]. I campioni di metacinabro provenienti dalla Toscana meridionale non mostrano invece significative sostituzioni chimiche. Il metacinabro della miniera di Niccioleta è stato identificato unicamente sulla base del diffrattogramma di polveri a causa della natura microcristallina del materiale disponibile; il parametro di cella, raffinato sulla base dei dati di polvere, è a = 5.859(1) Å. I campioni del distretto mercurifero del Monte Amiata provengono dalle miniere di Bagnore e Pietrineri. I parametri di cella raffinati sulla base di dati di cristallo singolo sono a = 5.8358(14) Å (Bagnore) e 5.8355(5) Å (Pietrineri). I raffinamenti strutturali per i campioni di Bagnore e Pietrineri convergono a fattore di accordo R_1 = 0.037 e 0.026, rispettivamente. La presenza di metacinabro nelle mineralizzazioni toscane può essere interpretata come evidenza di condizioni di temperatura relativamente elevata (> 315°C) raggiunte localmente durante la formazione dei depositi mercuriferi.

Parole chiave - metacinabro, struttura cristallina, mercurio, solfuro, Alpi Apuane, Monte Amiata, Colline metallifere, Toscana, Italia

Introduction

Metacinnabar is the high T polymorph of HgS, stable above 315-345°C (at 1 bar) depending of the sulfur fugacity of the crystallization environment (*e.g.*, Potter & Barnes, 1978; Sharma *et al.*, 1993). At higher T (above 470-481°C), metacinnabar inverts to hypercinnabar, the hexagonal form of HgS. Such variable transition temperatures are mainly controlled by fS_2 and by the non perfect stoichiometry behavior of HgS (Potter & Barnes, 1978). Stoichiometric HgS (*i.e.*, Hg/S atomic ratio = 1) is stable at relatively low fS_2 and the cinnabar-metacinnabar transition occurs at 345°C. At higher fS_2, HgS becomes progressively Hg-deficient (*i.e.*, Hg/S atomic ratio down to 0.86) and, in the presence of S excess in the system, the cinnabar-metacinnabar transition temperature decrease to 315°C. Experiments performed at variable T-P conditions and in both HgS and HgS-ZnS systems indicate that the cinnabar-metacinnabar transition temperature increaseas at high P, whereas it is lowered by the substitution of Hg by Zn and/or Fe (*e.g.*, Tauson & Abramovich, 1980; Tauson *et al.*, 1984). Cinnabar rarely contains traces of other metals, whereas the crystal structure of metacinnabar is able to host several other elements, *e.g.*, up to 9 mol% ZnS and 2 mol% FeS. In this latter case, metacinnabar may crystallize at low P for T around 200-250°C (Tauson *et al.*, 1984). Finally, metacinnabar precipitates at very low T in anoxic soils and sediments under controlled conditions in presence of organic matter (*e.g.*, Gerbig *et al.*, 2011 and references therein). In spite of such a complex behaviour, the occurrence of metacin-

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nabar may provide some insights about the conditions of crystallization in ore deposits (*e.g.*, Dini *et al.*, 1995). Metacinnabar was first described by Moore (1870) from the Redington mine, Hapa Co., California, USA, and later reported from several occurrences worldwide. The first identification of metacinnabar from Tuscany was reported by D'Achiardi (1876) from the Levigliani mine, Apuan Alps. This occurrence was later studied by Manasse (1921) and further investigated by Dini (1995) and Dini *et al.* (1995). Recently, Biagioni & Orlandi (2009) reported the finding of Se-rich metacinnabar closely associated with S-rich tiemannite from the Buca della Vena mine, Apuan Alps.

In addition to the findings from the hydrothermal veins of Apuan Alps, metacinnabar has been reported from other Tuscan occurrences. In particular, Arisi Rota *et al.* (1971) and Betti & Pagani (2000) reported the presence of this mineral in the Monte Amiata Hg ore district, whereas recently Bazzoni *et al.* (2015) gave a brief description of metacinnabar from the Niccioleta mine, in the Metalliferous Hills region. As a matter of fact, whereas the findings from the Apuan Alps have been characterized through X-ray diffraction and chemical analyses, no mineralogical data were given to support the occurrence of metacinnabar from the Niccioleta mine and the Monte Amiata Hg ore district. The aim of this paper is to fill this gap, reporting crystallographic data on selected specimens of metacinnabar from southern Tuscany; in addition single-crystal X-ray diffraction data on specimens from the Levigliani mine are given, completing the characterization of such a finding.

Experimental

Eight specimens labeled as metacinnabar were studied (Table 1). Their identification was initially performed through X-ray powder diffraction, using a 114.6 mm Gandolfi camera and Cu*K*α radiation. In this first step, three specimens turned out to be mislabeled, being actually cinnabar and not the cubic dimorph metacinnabar (samples #1153, #1156, and #1157 from Morone and Abbadia San Salvatore mines). The remaining specimens were identified as metacinnabar and were further characterized through qualitative EDS chemical analyses, carried out with a Philips XL30 scanning electron microscope equipped with an EDAX DX4 system. Specimens from Levigliani, Bagnore, and Pietrineri mine were suitable for single-crystal X-ray diffraction, which was carried out by using a Bruker Smart Breeze diffractometer coupled with an air-cooled CCD area detector and graphite-monochromatized Mo*K*α radiation. Intensity data collections were performed with a detector-to-crystal distance of 50 mm. Data were corrected for Lorentz-polarization factor and for absorption using the package of software *Apex*2 (Bruker AXS, 2004). The crystal structures have been refined using *Shelxl*-2014 (Sheldrick, 2015) starting from the atomic coordinates given by Wyckoff (1963). Details of data collections and crystal structure refinements are given in Table 2.

Metacinnabar from Tuscany: New data

Metacinnabar belongs to the sphalerite group. Its crystal structure was first solved by Lehmann (1924). It shows two independent atomic sites, *i.e.* Hg at (0, 0, 0) and S at (¼, ¼, ¼). Mercury is tetrahedrally coordinated by S; similarly, each S atom lies at the center of a regular tetrahedron of Hg atoms. In metacinnabar, Hg can be replaced by minor amounts of other divalent metal cations, such as Zn, Fe, Mn, and Cd. Sulfur can be substituted by Se and Te; when the substitution is greater than 50 at%, the isostructural minerals tiemannite (HgSe) and coloradoite (HgTe) occur. These substitutions affect the unit-cell parameter and the metal-anion distance. According to the bond parameters given by Brese & O'Keeffe (1991), the ideal metal-S distance in a regular tetrahedron decreases following the sequence (ideal distance in Å/metal): 2.576/Hg^{2+},

Table 1 - Details of the specimens studied.

Label	Description	Locality
#617	metallic black, with conchoidal fracture, associated with cinnabar	Galleria Lunga, Levigliani mine, Apuan Alps
#621	black tetrahedral crystals in calcite, with marcasite and sphalerite	Bagnore mine, Amiata
#626	metallic black	Speranza, Levigliani mine, Apuan Alps
#815	tetrahedral black crystals with cinnabar	Pietrineri mine, Amiata
#1026	anhedral black grains with cinnabar, galena and sphalerite	Niccioleta mine
#1153	black crusts with microcrystalline cinnabar	Morone mine, Amiata
#1156	black grains with cinnabar	Abbadia San Salvatore, Amiata
#1157	equant black-reddish crystals	Morone mine, Amiata

Table 2 - Details of data collection, crystal structure refinements, and structural features of selected metacinnabar samples.

CRYSTAL DATA			
Sample label – Locality	#617 – Levigliani mine	#621 – Bagnore mine	#815 – Pietrineri mine
Crystal size (mm)	0.18 × 0.16 × 0.09	0.15 × 0.12 × 0.08	0.18 × 0.16 × 0.11
Cell setting, space group		Cubic, $F\bar{4}3m$	
a (Å)	5.7966(8)	5.8358(14)	5.8355(5)
V (Å^3)	194.77(8)	198.75(14)	198.72(5)
Z		4	
DATA COLLECTION AND REFINEMENT			
Radiation, wavelength (Å)		Mo$K\alpha$, 0.71073	
Temperature (K)		293	
$2\theta_{max}$ (°)	64.14	63.65	63.66
Measured reflections	81	128	130
Unique reflections	43	46	50
Reflections with $F_o > 4\sigma(F_o)$	43	46	50
R_{int}	0.0253	0.0393	0.0398
$R\sigma$	0.0450	0.0376	0.0509
Range of h, k, l	$-3 \le h \le 5$, $-3 \le k \le 6$, $-8 \le l \le 0$	$-6 \le h \le 6$, $-6 \le k \le 4$, $-8 \le l \le 4$	$-4 \le h \le 7$, $-8 \le k \le 2$, $-6 \le l \le 6$
R (all data)	0.0443	0.0371	0.0256
wR (on F_o^2)	0.1085	0.0978	0.0638
Goof	1.395	1.269	1.272
Number of least-squares parameters	6	5	5
Maximum and minimum residual peak (e Å^{-3})	2.93 (at 1.17 Å from Hg) -2.94 (at 1.96 Å from Hg)	2.33 (at 2.53 Å from S) -1.64 (at 1.01 Å from Hg)	1.41 (at 0.00 Å from Hg) -0.97 (at 1.18 Å from Hg)
STRUCTURAL FEATURES			
Hg site occupancy factor	$Hg_{0.91(1)}Zn_{0.09(1)}$	$Hg_{1.00}$	$Hg_{1.00}$
Hg-S (Å)	2.5100(3)	2.5270(6)	2.5268(2)
U_{eq} Hg site (Å^2)	0.0234(16)	0.0318(14)	0.0310(9)
U_{eq} S site (Å^2)	0.010(5)	0.019(3)	0.0168(18)

Note: the equivalente isotropic displacement parameter U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2.546/Cd^{2+}, 2.456/Mn^{2+}, 2.416/Fe^{2+}, and 2.346/Zn^{2+}. Metacinnabar samples from Tuscany are usually close to the ideal endmember composition HgS; the only exception is represented by (Zn,Fe)-rich specimens from the Levigliani mine, as described by previous authors (*e.g.*, Dini *et al.*, 1995). In the binary system ZnS-HgS, Tauson & Abramovich (1980) proposed a relation between the *a* unit-cell parameter and the mol% HgS, *i.e.* $a = 5.409 + 0.00442$ mol% HgS. End-member metacinnabar should have a theoretical *a* parameter of 5.851 Å. No hints for the replacement of S by heavier atoms (*e.g.*, Se, Te) have been observed in the studied specimens, even if Se-rich metacinnabar is known from the Buca della Vena mine (Biagioni & Orlandi, 2009).

In the following, the description of the specimens studied and the results of their mineralogical characterization are given.

Levigliani mine, Apuan Alps

As reported above, the occurrence of metacinnabar from this locality has been known since the 19th Century (D'Achiardi, 1876) and was fully confirmed by Dini (1995) and Dini *et al.* (1995) through X-ray powder diffraction and electron-microprobe analysis.
The two studied specimens were sampled in the Galleria Lunga (#617) and Speranza (#626) stopes. The former is represented by an intergrowth of cinnabar and black metallic metacinnabar in a quartz-carbonate vein; the latter has small black shiny metallic anhedral grains of metacinnabar, with a conchoidal fracture, in a quartz vein. Sample #617 was used for the single-crystal X-ray diffraction study. Its refined unit-cell parameter, a = 5.7966(8) Å, agrees with the one reported by Dini (1995) on the basis of X-ray powder diffraction, *i.e.* a = 5.815 Å. According to the relation proposed by Tauson & Abramovich (1980), the studied sample should correspond to an HgS mol content in the range 88-92 mol%.
The site scattering value refined at the Hg site, *i.e.* 75.5 electrons per formula unit (*epfu*), agrees with the one calculated on the basis of the electron-microprobe analyses given by Dini *et al.* (1995), *i.e.* 75.4 epfu. The proposed site population at the Hg site of metacinnabar from Levigliani is $(Hg_{0.91}Zn_{0.07}Fe_{0.02})$. On the basis of such a population, a theoretical Hg-S bond distance of ~2.557 Å should be expected. The observed value is shorter, *i.e.* 2.5100(3) Å. This discrepancy is probably related to the inaccurate value of the bond valence parameter for the Hg-S bond given by Brese & O'Keeffe (1991) and to the covalent nature of this bond in metacinnabar.

Bagnore mine, Monte Amiata Hg ore district

The occurrence of metacinnabar from this locality was reported by Arisi Rota *et al.* (1971), who listed the minerals associated to cinnabar, *i.e.* pyrite, marcasite and very small amount of metacinnabar, realgar, orpiment, and native mercury.
The studied specimen was bought from the mineral collectors Andrea and David Ulivi. Metacinnabar occurs as black tetrahedral crystals in a calcite vein embedded in sandstone. Associated minerals are marcasite, in µm-sized thin tabular metallic golden yellow crystals, and yellow equant individuals of sphalerite (Fig. 1). Qualitative EDS chemical analysis did not show any element with $Z > 9$ other than Hg and S above the detection limit. The refined unit-cell parameter is a = 5.8358(14) Å; using the Tauson & Abramovich (1980) relationship, it could correspond to a composition close to ~97 mol% HgS, in agreement with site scattering values refined at the Hg site, indicating a pure Hg site population. The observed Hg-S value is 2.5270(6) Å.

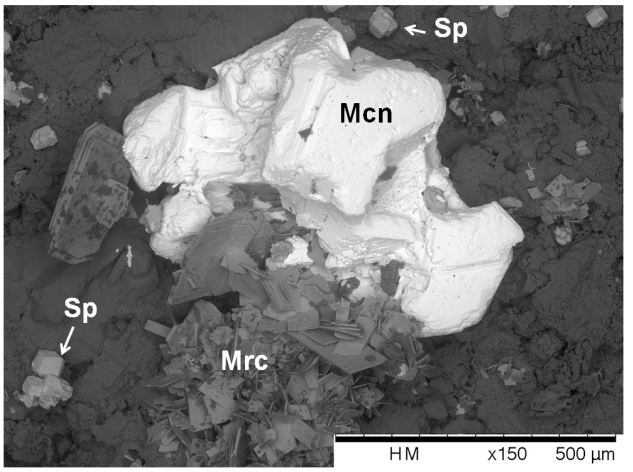

Fig. 1 - Metacinnabar (**Mcn**), aggregates of rounded tetrahedral crystals associated with thin tabular crystals of marcasite (**Mrc**) and small equant crystals of sphalerite (**Sp**). Bagnore mine, Monte Amiata Hg ore district. BSE image, photo C. Biagioni.

Pietrineri mine, Monte Amiata Hg ore district

The presence of metacinnabar from the Pietrineri mine (Bagni San Filippo) was previously reported (*e.g.*, Meli, 2002), even if an accurate description of this finding was lacking.
The studied specimen was kindly provided by the mineral collector Simone Beccari. It is represented by a breccia with fragments of quartz (in some cases in euhedral bipyramidal crystals, colorless to brownish in color) and microcrystalline cinnabar, in a gangue formed by calcite. Large prismatic crystals of celestine occur in the same sample. Through the use of diluted HCl, calcite was removed and the occurrence of small cavities lined by mm-sized rhombohedral crystals of cinnabar and black triacistetrahedral individuals of metacinnabar was shown. The refined unit-cell parameter, a = 5.8355(5) Å, and the Hg-S distance [2.5268(2) Å] are close to those observed in the specimen from Bagnore, agreeing with the occurrence of Hg and S as the only elements above the detection limit. As it happens for the specimen from Levigliani, the observed Hg-S distances in both samples from Monte Amiata are shorter than the theoretical one, calculated on the basis of the bond parameters given by Brese & O'Keeffe (1991).

Niccioleta mine, Metalliferous Hills ore district

The Niccioleta mine is well-known world-wide for the beautiful specimens of pyrite found during the mining activity (*e.g.*, Brizzi *et al.*, 1989; 1990a, 1990b). Bazzoni *et al.* (2015) reported the occurrence of metacinnabar from this locality, describing it as microcrystalline black crusts with cinnabar and pyrite on calcite; sphalerite and galena occur as disseminated crystals

within calcite. The mineral collector Cristiano Bazzoni kindly provided us with a specimen of metacinnabar from this locality. Scanning electron microscope study revealed that the microcrystalline aggregates are actually formed by μm-sized tetrahedra of metacinnabar, with a distinct conchoidal fracture. Owing to the small size of these crystals, only the X-ray powder diffraction pattern was collected. The refinement of the unit-cell parameter using the software *UnitCell* (Holland & Redfern, 1997) gave $a = 5.859(1)$ Å. Qualitative EDS analysis showed Hg and S as the only elements with $Z > 9$ above the detection limit.

Discussion

The present study confirms the occurrence of metacinnabar in the hydrothermal ores from the Monte Amiata Hg ore district and completes the crystal-chemical characterization of metacinnabar from the Levigliani mine, reporting the results of a crystal structure refinement.

Samples from Apuan Alps have a more complex crystal-chemistry with respect to the other Tuscan occurrences; this statement is further confirmed taking into account also the description of the tiemannite-metacinnabar solid solution from Buca della Vena (Biagioni & Orlandi, 2009). Indeed, Hg is partially substituted by Zn and Fe, whereas S can be replaced by Se. These substitutions reflects the complex and variable geochemistry of the hydrothermal ores from Apuan Alps. As pointed out by Dini *et al.* (2001), the metamorphic conditions of Apuan Alps provided ideal conditions for the mobilization of Hg. The association of this element with other metals (Cu, Zn, Ag, Tl, Pb) together with Sb (major), As (minor), and Bi (rare), as well as the occurrence of trace amounts of Se, Te, and Cl led to the formation of a large number of Hg species, among which five new Hg species (*i.e.*. grumiplucite, rouxelite, marrucciite, arsiccioite, and andreadiniite).

The relatively simple mineralogy shown by the Monte Amiata Hg deposits is the expression of a less variable ore geochemistry and of the typical "Hg-only" character of such deposits worldwide. This is reflected in the crystal-chemistry of metacinnabar, showing only Hg and S as elements above the detection limit. More intriguing is the simple composition of metacinnabar from the Niccioleta mine that, in spite of the dominance of pyrite (the main ore mineral), occurs in quite a complex sulfide-oxide-silicate mineral association.

The occurrence of metacinnabar should indicate relatively high T conditions. However, as already noted in the introduction, several chemical and physical parameters control the temperature of the cinnabar-metacinnabar transition. Accordingly, the occurrence of metacinnabar cannot be used as a well-calibrated geothermometer. As discussed by Dini *et al.* (1995, 2001), in the ore deposits of Apuan Alps the conditions for crystallization of Zn-rich metacinnabar were reached close to the metamorphic peak conditions, during the inception of the extensional stage. In this case, geological, petrological, textural, and chemical data fit well with information provided by hydrothermal experiments (*e.g.*, Tauson *et al.*, 1984), indicating high T and P. The occurrence of the cubic polymorph of HgS in the pyrite ore deposit of Niccioleta is not surprising, since the available fluid inclusion data are consistent with the stability field of metacinnabar. Belkin *et al.* (1983) reported fluid inclusion temperatures from the Niccioleta ore between 200 and 320°C; similar T values, ranging from 172 and 331°C, were proposed by Liotta *et al.* (2010) for the nearby Boccheggiano-Montieri area. These values are close to the cinnabar-metacinnabar transition (*i.e.*, 315-345°C). Consequently, the crystallization of metacinnabar at Niccioleta could be related to the high T stage of formation of such hydrothermal ores.

The metacinnabar occurrences in the Hg deposits from the Monte Amiata area are more problematic, because their pure HgS composition suggests a minimum crystallization T of 315-345°C under hydrothermal conditions. The few available fluid inclusion studies of such ore deposits indicate typical epithermal conditions, developed in a T range between 70 and 130°C near the surface (Brogi & Fabbrini, 2009; Gasparrini *et al.*, 2013). The discrepancy between the two temperature estimates can be explained in two different ways.

A first explanation involve the possibility that hot fluids, similar in temperature to those reported for the exploited geothermal field (300-360°C; Bertini *et al.*, 2005), have been locally involved in ore formation. Consequently, the occurrence of metacinnabar at the Bagnore and Pietrineri mines could be related to the local spilling of the deepest (and hottest) portion of the Monte Amiata hydrothermal system where T conditions favorable to the crystallization of metacinnabar could be achieved. Indeed, Bagnore is one of the areas still showing the highest T of the geothermal field (*e.g.*, Fulignati *et al.*, 2014).

A second possible explanation takes into account the observed metastable precipitation of metacinnabar mediated by dissolved organic matter. At the Bagnore mine, the presence of significant amounts of heavy liquid hydrocarbons and bitumen associated with the cinnabar ores is well known (Arisi Rota *et al.*, 1971). Hydrocarbons can play an important role in Hg transport in hydrothermal systems (Fein & Williams-Jones, 1997) and they could also create favorable conditions for the precipitation of metacinnabar in epithermal systems.

Unfortunately, owing to the lack of knowledge about the occurrence of the samples studied within the ore deposits and the very low number of examined specimens, the actual distribution of metacinnabar in the

Monte Amiata Hg ore district is not known. Some alleged occurrences reported by other authors (*e.g.*, Betti & Pagani, 2000) were checked and identified as cinnabar. Since the mining activity ceased some decades ago and the ore deposits are no more accessible, only the examination and the study of old specimens kept in mineralogical museums as well as in private mineral collections can provide material for further studies.

Acknowledgments

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